4-21-20

Canonical Ensemble : Ideal Gas

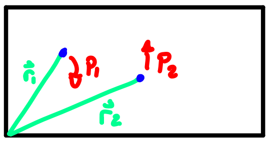
Need Z

$\hookrightarrow \bar{E} = -\frac{\partial}{\partial \beta} \ln(Z)$

$\bar{F} = -kT\ln(Z)$

$S = (\bar{E}-\bar{F})/T$

Purely classical particles in a box



Microstates for all particles

$\vec{r}_1, \vec{r}_2, \ldots\ldots$

$\vec{p}_1, \vec{p}_2, \ldots\ldots$

microstate for a single particle

$\vec{r}, \vec{p}$

Energy $E = \frac{1}{2m}\vec{p}^{\,2}$

issues : * counting with continuous variables.

* eventual issue with entropy

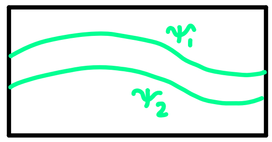
if $V \rightarrow \lambda V$

$N \rightarrow \lambda N$

is $S \rightarrow \lambda S$

* chemical potential ?

Semi-classical particles in a box



Microstates for all

$\psi_{p_1} = \cos \sin\left(\frac{n_{1x}\pi x}{L}\right)\sin\left(\frac{n_{1y}\pi y}{L}\right)\sin\left(\frac{n_{1z}\pi z}{L}\right)$

need n_{1x}, n_{1y}, n_{1z} Particle 1

n_{2x}, n_{2y}, n_{2z} Particle 2

microstate for single particle

n_x, n_y, n_z

Energy $E = \frac{h^2}{8mL^2}(n_x^2+n_y^2+n_z^2)$

issues : * count n_x, n_y, n_z

* statistics of quantum particles

* chemical potential ?

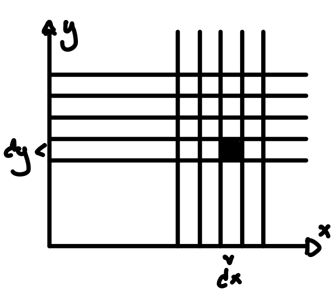
Will get : * Energy eqn of state

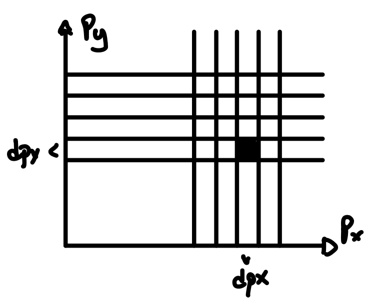
* Pressure eqn of state

* Probability with which various states + velocities occur

Classical Description

Single classical particle in a box. Need to create a discrete grid for states





State consists of :

1) choosing $dx, dy, dz, dpx, dpy, dpz$ to create grid
2) one box (cell) from each grid

Energy

$E = \frac{1}{2m}(P_x^2+P_y^2+P_z^2)$

Canonical Ensemble

1) Partition Function (single particle)

$$Z_{single} = \sum e^{-(p_x^2+p_y^2+p_z^2)/2m\,\beta}$$

2) Probability particle in state

$$e^{-E\beta}/Z_{single} = \frac{e^{-(p_x^2+p_y^2+p_z^2)\beta/2m}}{Z_{single}}$$

Need to consider grid size $\to$ 0. Sums become integrals

$$Z = \alpha \int_0^L dx \int_0^L dy \int_0^L dz \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \; e^{-(p_x^2+p_y^2+p_z^2)\beta/2m}$$

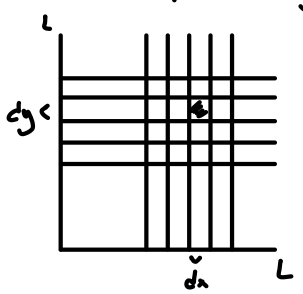
Need Z to have no physical dimensions. Integrals give
$m^3 (kg\, m/s)^3$

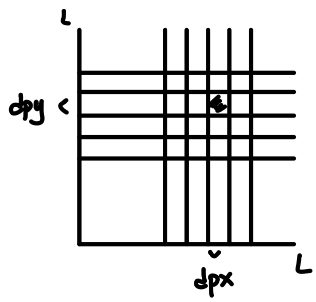
Need α to eliminate these, α has dimensions
$m^{-3}(kg\, m/s)^{-3}$

4-28-20

Classical ideal gas via canonical ensemble

States are represented by a discrete state space





$$E = \frac{1}{2m}(p_x^2+p_y^2+p_z^2)$$

Single particle partition function

$$Z_{single} = \sum_i \frac{e^{-E_i\beta}}{Z} = \alpha \int dx \int dy \int dz \int dp_x \int dp_y \int dp_z \; e^{-(p_x^2+p_y^2+p_z^2)\beta/2m}$$

Semi classical Canonical Ensemble Approach

Each particle ~ quantum particle in infinite 3-dimensional well
~ Cubic well sides L

Energy states labeled by $n_x, n_y, n_z = 1, 2, 3, 4 \ldots$

energy $E = \frac{h^2}{8mL^2}(n_x^2+n_y^2+n_z^2)$

Partition Function single particle:

$$Z_{single} = \sum_{\text{all states}} e^{-E_s\beta} = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} e^{-n_x^2h^2\beta/8mL^2}\, e^{-n_y^2h^2\beta/8mL^2}\, e^{-n_z^2h^2\beta/8mL^2}$$

$$= \sum_{n_x=1}^{\infty} e^{-n_x^2h^2\beta/8mL^2} \sum_{n_y=1}^{\infty} \cdots\cdots$$

$$Z_{single} = \left[\sum_{n=1}^{\infty} e^{-n^2h^2\beta/8mL^2}\right]^3$$

Need $S = \sum_{n=1}^{\infty} e^{-n^2 h^2 \beta / 8mL^2}$ approximate via integral $\int e^{-n^2 \cdots} dn$

Consider $\frac{h^2\beta}{8mL^2} = \frac{h^2}{8mkT} \frac{1}{L^2}$

Let $\alpha^2 = \frac{h^2\beta}{8mL^2} << 1$ $\alpha = \sqrt{\frac{h^2\beta}{8mL^2}} << 1$ $S = \sum_{n=1}^{\infty} e^{-\alpha^2 n^2} = \int_0^{\infty} e^{-\alpha^2 n^2} dn = \frac{1}{2}\sqrt{\frac{\pi}{\alpha^2}} = \frac{1}{2\alpha}\sqrt{\pi}$

$S = \ldots\ldots = \sqrt{\frac{mL^2}{2\pi\hbar^2\beta}}$ $\hbar = \frac{h}{2\pi}$ $Z_{single} = \left[\frac{mL^2}{2\pi\hbar^2\beta}\right]^{3/2} = V\left[\frac{m}{2\pi\hbar^2\beta}\right]^{3/2}$

$Z = (Z_{single})^N = V^N\left[\frac{m}{2\pi\hbar^2\beta}\right]^{3N/2}$: $\bar{E} = -\frac{\partial}{\partial\beta}\ln(Z) \Rightarrow \bar{E} = \frac{3}{2}NkT$

$P = -\frac{\partial F}{\partial V} = kT\frac{\partial}{\partial V}\ln(Z) \Rightarrow PV = NkT$

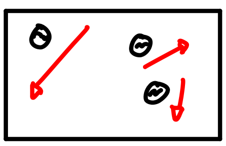
$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \ldots\ldots \Rightarrow \mu = -kT\left[\ln(V) + \ln\left(\frac{m}{2\pi\hbar^2}\right)^{3/2} + \frac{3}{2}\ln(kT)\right]$

Velocity Probability Distribution

Gas consisting of many identical particles. Gas is at temperature T.

- info about velocity / speed

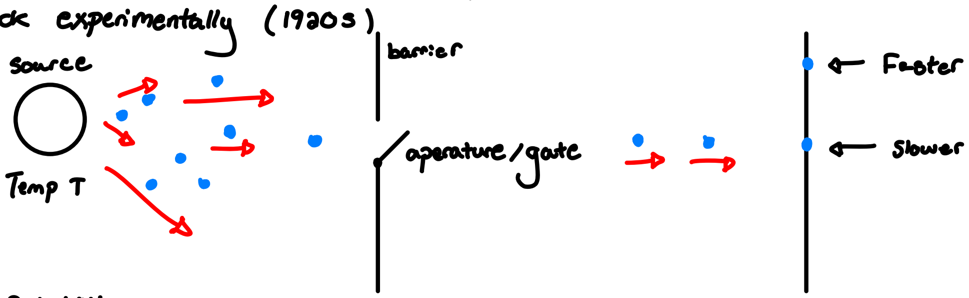
$\bar{E} = \frac{3}{2}NkT$

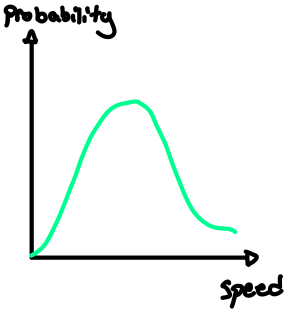


- velocity / speed varies by molecule
- want
  * Probability distribution of velocities?
  * " " " " speeds?
  * Mean speed?

Canonical ensemble $\rightsquigarrow$ theoretical predictions

Check experimentally (1920s)





using the canonical ensemble: If s is state of a gas particle, E_s is energy then probability with which this state occurs is

$P_s = A e^{-E_s\beta}$

where $\beta = 1/kT$ and $A = 1/Z$ is constant

Here state depends on velocity + position

$E_s \to (P_x^2+P_y^2+P_z^2)/2m = \frac{1}{2} m(v_x^2+v_y^2+v_z^2)$

Molecule has velocity

$$\text{Prob}\,[\vec v \to \vec v + d^3\vec v] = \left[\frac{m\beta}{2\pi}\right]^{3/2} e^{-(v_x^2+v_y^2+v_z^2)m\beta/2}\, dv_x\, dv_y\, dv_z$$

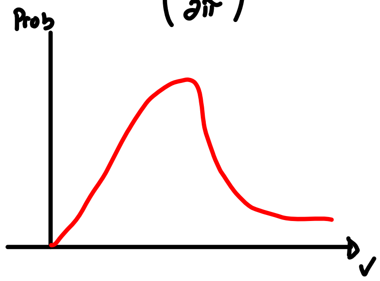
Distribution of speeds

Prob (Speed is in range $v \to v+dv$) $= 4\pi\left(\frac{m\beta}{2\pi}\right)^{3/2} v^2 e^{-v^2 m\beta/2}\, dv$

regardless of direction

Maxwell probability distribution for speeds

$$P(v) = 4\pi \left(\frac{m\beta}{2\pi}\right)^{3/2} v^2 e^{-v^2 m\beta/2}$$



1) Most prob. velocity $\frac{dP}{dv} = 0$

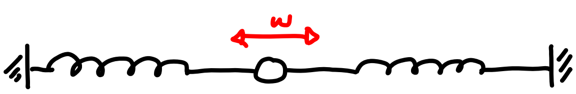
2) Mean velocity $\bar v = \int_0^\infty v P(v)\, dv$

3) Mean KE via $\bar{v^2} = \int_0^\infty v^2 P(v)\, dv$

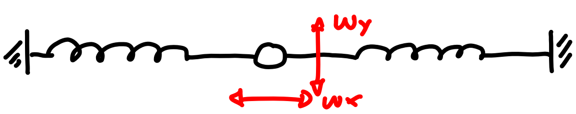
4-30-20

Classical oscillators

- Use canonical ensemble
- Some possibilities
  1) one dimensional oscillator



  2) Two or three dimensional oscillators
  - Assume oscillators are distinguishable
  - Get partition function for single particle



Integrals to get Z often involve $\int_{-\infty}^{\infty} e^{-u^2\alpha\beta}\, du \longrightarrow \sqrt{\frac{\pi}{\alpha\beta}}$

If there are n such terms then $Z = \text{const} \times \beta^{-n/2}$

$\ln(Z) = \ln[\text{const}] - n/2 \ln(\beta)$

$\bar E = -\frac{\partial}{\partial\beta}\ln(Z) = \frac{n}{2}\cdot\frac{1}{\beta} \Rightarrow \bar E = \frac{n}{2}kT$

Suppose energy of system depends on n variables $u_1, \dots, u_n$ and is quadratic

$E_{state} = \alpha_1 u_1^2 + \dots + \alpha_n u_n^2 \longrightarrow Z = \text{const} \times \beta^{-n/2} \to \bar E = \frac{n}{2}kT \to C = \frac{n}{2}k$

This gives equipartition theorem:

If a classical system has an energy quadratic in n independent variables and is in equilibrium with a bath at temp T then

$$\bar{E} = \frac{n}{2} kT$$

e.g. N three dimensional oscillators (classical) then $n = 6N \Rightarrow \bar{E} = 3NkT \rightsquigarrow C = 3Nk$

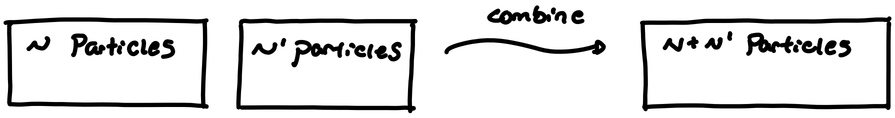
Dulong Petit Law

e.g. one mole $3 \times N_A \times k = 3 \times 8.314 \approx 25$ J/k

Entropy + Systems of distinguishable particles

Canonical Ensemble $\rightsquigarrow$ entropy $\rightsquigarrow$ is this extensive?

Extensive considers properties when system size changes.



Expect that:

* Volume add $V(N+N') = V(N) + V(N')$
* Energy " $E(N+N') = E(N) + E(N')$
* Entropies " $S(N+N') = S(N) + S(N')$

True for all N, N' - only way is if

$$\left.\begin{aligned} V(\lambda N) &= \lambda V(N) \\ E(\lambda N) &= \lambda E(N) \\ S(\lambda N) &= \lambda S(N) \end{aligned}\right\} \text{Extensive}$$

By definition $\rho = N/V$ is same $V = N/\rho$

Canonical ensemble $\rightsquigarrow$ partition function:

$$Z = \left(\frac{m}{2\pi\hbar^2}\right)^{3N/2} V^N \beta^{-N/2}$$

$\bar{E} = -\frac{\partial}{\partial \beta} \ln(Z) \rightsquigarrow \bar{E} = \frac{3}{2} NkT$: if $N \to \lambda N$ $\bar{E} \to \lambda \bar{E}$

entropy $S = -\frac{\partial F}{\partial T} = -\frac{\partial}{\partial T}[-kT\ln(Z)]$

$$S = Nk\left\{\ln\left(\frac{m}{2\pi\hbar^2}\right)^{3/2} + \ln(V) - \frac{3}{2}\ln(\beta)\right\} + \frac{3}{2}Nk$$

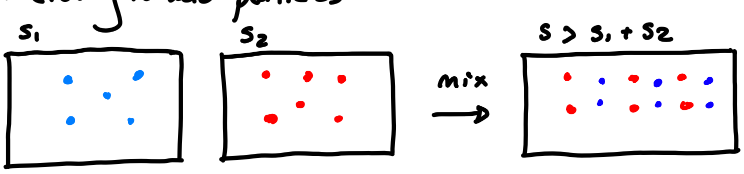
Suppose $N \to \lambda N$, $V \to \lambda V$, $\bar{E} \to \lambda \bar{E}$

$$S \to \lambda\left[Nk\left\{\ln\left(\frac{m}{2\pi\hbar^2}\right)^{3/2} + \ln(V) - \frac{3}{2}\ln(\beta)\right\} + \frac{3}{2}Nk\right] + \lambda Nk\ln[\lambda]$$

$S \to \lambda S + \lambda Nk \ln(\lambda) \longleftarrow$ Not extensive

Assuming ensemble of distinguishable particles, canonical ensemble gives entropy that is not extensive

Issue: distinguishable particles

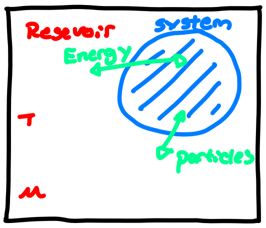


Need to consider indistinguishable particles. Difficulty

$$Z_{N\,particle} \neq (Z_{single})^N$$

Grand Canonical Ensemble

- generalization of canonical ensemble
- now system can exchange particles with resevoir
- Then can show:



List states of system - "s"

- Energy E_s
- Particle number N_s $\longrightarrow$ Probability particle in state "s"

$$p_s = \frac{1}{Z_G} e^{-(E_s - \mu N_s)\beta}$$

where grand partition function

$$Z_G = \sum e^{-(E_s - \mu N_s)\beta}$$

Mean particle number : Mean Energy

$$\bar{N} = \frac{1}{\beta}\frac{\partial}{\partial \mu} \ln[Z_G] \qquad \bar{E} = -\frac{\partial}{\partial \beta}\ln[Z_G] + \mu \bar{N}$$

Connect to thermodynamics system particle number $N \equiv \bar{N}$, system energy $E \equiv \bar{E}$

Grand canonical ensemble: Indistinguishable Particles

Example: Single particle has two states $\rightsquigarrow$ energy $0, \epsilon$.

Single Particle/system	Energy
$k=1$ (lower energy state)	$\epsilon_1 = 0$
$k=2$ (higher energy state)	$\epsilon_2 = 1$

State of ensemble described by occupation number

n_k = number of ensemble members in single particle state k

State of ensemble is described by

$$S \equiv (n_1, n_2, n_3, \ldots\ldots)$$

in state S

$$N = n_1 + n_2 + n_3 + \ldots\ldots \qquad N_s = \sum_i n_k$$

$$E_s = n_1\epsilon_1 + n_2\epsilon_2 + \ldots\ldots \qquad E_s = \sum_i n_k \epsilon_k$$

5-5-20

Grand Canonical Ensemble

- States have variable energy + particle number
- State "s"

Energy E_s
Particle number N_s

- Grand partition function
  $Z_G = \sum e^{-(E_S - \mu N_S)\beta}$
  $\downarrow$

  Mean particle number
  $\bar{N} = \frac{1}{\beta}\frac{\partial}{\partial \mu} \ln[Z_G]$

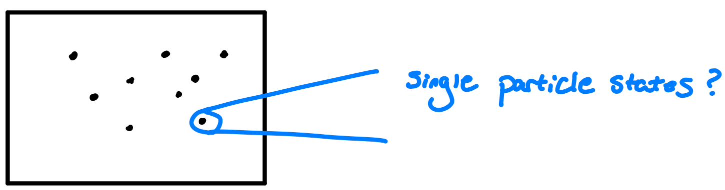
  Mean energy
  $\bar{E} = -\frac{\partial}{\partial \beta}\ln[Z_G] + \mu\bar{N}$

- want to reformulate this in terms of single particle states
- Label these states by "k" $\longrightarrow$ Energy ϵ_k
- Occupation number n_k = number of particles in state k
- then "S" = $[n_1, n_2, n_3, \ldots]$

  $E_S = \sum_k n_k \epsilon_k \qquad N_S = \sum_k n_k$

  $Z_G = \sum_{n_1 n_2 \ldots} e^{-(\epsilon_1 n_1 - \mu n_1)\beta} e^{-(\epsilon_2 n_2 - \mu n_2)\beta} \ldots\ldots$

Scheme: System of indistinguishable particles



Describe all single particle states

$k=3$ ______ ϵ_3

$k=2$ ______ ϵ_2

$k=1$ ______ ϵ_1

$\downarrow$

Grand partition function is: $\prod_n^\infty Z_{G_n}$ where single state partition function ..... $Z_{Gk} \sum_{n_k}^{\infty} e^{-(\epsilon_k - \mu)n_k\beta}$

$\downarrow$

Mean occupation number of state k is:

$\bar{n}_k = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln[Z_{Gk}]$

$\downarrow$

Mean particle number $\longrightarrow$ Mean Energy

$\bar{N} = \sum \bar{n}_k \qquad \bar{E} = \sum \epsilon_k \bar{n}_k$

Quantum physics - two categories of particle system

1) Bosons – unlimited number of particles can be in any single state
   - Bose-Einstein Statistics
   - e.g. photons, paired electrons, spin 0,1,2,3 .... particles
2) Fermions - at most one particle can be in any single state
   - Fermi-Dirac statistics
   - electrons, protons, spin 1/2, 3/2, ...

<u>Bose-Einstein</u>

For any single state k

$n_k = 0,1,2,3,\ldots \to \infty \qquad Z_{Gk} = \sum e^{-n_k(\epsilon_k - \mu)\beta}$

Fermi-Dirac

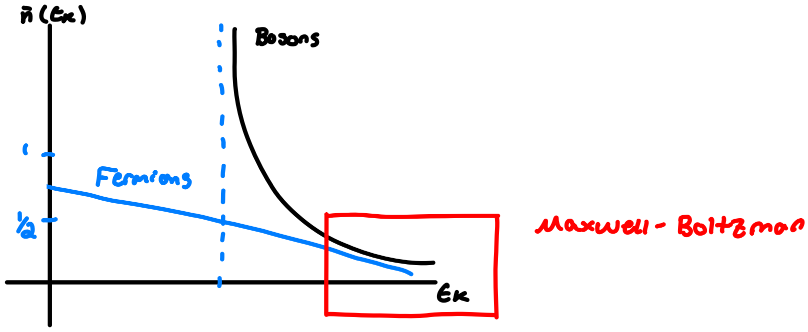
For any single state k

$n_k = 0, 1$

Then:

Bosons	$\bar{n}_k(\epsilon_k) = 1/e^{(\epsilon_k-\mu)\beta}-1$ if $\epsilon_k > \mu$
Fermions	$\bar{n}_k(\epsilon_k) = 1/e^{(\epsilon_k-\mu)\beta}+1$ all ϵ_k, μ

Graph



Maxwell-Boltzman statistics

$(\epsilon_k - \mu)\beta >> 0$

$$\bar{n}_k(\epsilon_k) = e^{-(\epsilon_k-\mu)\beta}$$

Grand Canonical Ensemble and Entropy

So Far:

Single State partition Function:

Z_{ϵ_k}

$\downarrow$

Grand partition Function

$Z = Z_{\epsilon_1} Z_{\epsilon_2} \cdots\cdots$

$\downarrow$

Mean Energy $\bar{E}$, Mean particle number $\bar{N}$

Perhaps can relate $\bar{E}$ to $\bar{N}, T \longrightarrow$ energy equation of state.

Pressure equation of state? $\longrightarrow$ need S

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{N,E}$$

Need entropy for grand canonical ensemble:

For grand canonical ensemble:

$$S = k\ln[Z_G] + \frac{1}{T}(\bar{E} - \mu\bar{N}) = k\ln[Z_G] - \frac{1}{T}\frac{\partial}{\partial\beta}\ln(Z_G)$$

where

$$\bar{N} = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln[Z_G] \; ; \; \bar{E} = \mu\bar{N} - \frac{\partial}{\partial\beta}\ln[Z_G]$$

In terms of single state partition functions: $Z_{G_1}, Z_{G_2} \ldots$?

Can show

$$S = k\sum \ln[Z_{G_j}] + \frac{1}{T}(\bar{E} - \mu\bar{N})$$

where $\bar{N} = \sum \bar{n}_j$

$\bar{E} = \sum \epsilon_j \bar{n}_j \qquad \bar{n}_j = \sum e^{-n_j(\epsilon_j-\mu)\beta}$

Then:

1) Bose-Einstein $\quad \bar{n}_j = \dfrac{1}{e^{(\epsilon_j-\mu)\beta}-1} \quad \epsilon_j > \mu$

Bosons $S = k\sum_j \ln(1+\bar{n}_j) + \frac{1}{T}(\bar{E} - \mu\bar{N})$

Fermions: $S = -k\sum_j \ln(1-\bar{n}_j) + \frac{1}{T}(\bar{E} - \mu\bar{N})$

Maxwell - Boltzman $(\epsilon_j - \mu)\beta >> 0$ $\quad \bar{n}_j << 1$

$\ln(1+\bar{n}_j) \approx \bar{n}_j$ $\quad S = k\sum \bar{n}_j + \frac{1}{T}(\bar{E} - \mu\bar{N})$

$\ln(1-\bar{n}_j) \approx -\bar{n}_j$

$$S = k\bar{N} + \frac{1}{T}(\bar{E} - \mu\bar{N})$$

5-7-20

Grand Canonical Ensemble for Ideal Gas

Grand Canonical Ensemble

1) List single particle states ~ label j
   ~ energy ϵ_j
2) Mean occupation number
   $\bar{n}_j = \bar{n}_j(\epsilon_j)$
3) Mean energy $\bar{E} = \sum \bar{n}_j \epsilon_j$
4) Mean particle number
   $\bar{N} = \sum \bar{n}_j$
5) Entropy $S = k\sum \ln[Z_{G_j}] + 1/T(\bar{E} - \mu\bar{N})$

Three Distributions

1) Bos-Einstein $\quad \bar{n}_j(\epsilon_j) = 1/e^{(\epsilon_j - \mu)\beta} - 1$
2) Fermi - Dirac $\quad \bar{n}_j(\epsilon_j) = 1/e^{(\epsilon_j - \mu)\beta} + 1$
3) Maxwell - Boltzman $\quad \bar{n}_j(\epsilon_j) = e^{-(\epsilon_j - \mu)\beta}$ $\quad \bar{n}_j << 1$

Maxwell Boltzman

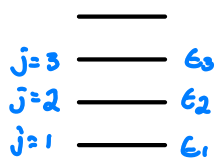
$S = k\bar{N} + 1/T(\bar{E} - \mu\bar{N})$

Mean Energies + particle numbers in terms of state energies

$\bar{N} = \sum \bar{n}_j(\epsilon_j)$

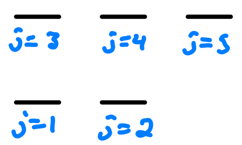
Non-degenerate case

No two states have same energy



Degenerate case

There are at least two states with same energy



$\bar{N} = \sum \bar{n}(\epsilon)$, single particle energies

$\bar{E} = \sum \epsilon\, \bar{n}(\epsilon)$

Energy does not label states we

$g(E)$ = number of states being used

$\bar{N}(E) = \sum g(\epsilon)\bar{n}(\epsilon)$

$\bar{E} = \sum \epsilon\, g(\epsilon)\bar{n}(\epsilon)$

$$\bar{N} = \int \bar{n}(\epsilon) g(\epsilon)\, d\epsilon \;,\quad \bar{E} = \int \epsilon\, \bar{n}(\epsilon) g(\epsilon)\, d\epsilon$$

Semi-classical model of ideal gas

1) Identical, indistinguishable particles in 3 dimensional cubic infinite well sides L
2) dilute $\bar{n}(\epsilon) << 1$ for any state

Single particle states + energy

States labeled by $n_x, n_y, n_z = 1, 2, 3, 4 \ldots$.

energy

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

Degenerate cases $\rightsquigarrow$ need $g(\epsilon)$

- note energy only depends on $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$

$$\epsilon(n) = \frac{\hbar^2 \pi^2}{8mL^2} n^2$$

- density of states ?

First $\Gamma(n)$ = number of states where $\sqrt{n_x^2 + n_y^2 + n_z^2} \leq n$ $\longrightarrow$ $g(n) = \frac{d\Gamma(n)}{dn}$ $\longrightarrow$ $g(\epsilon) = g(n) \frac{dn}{d\epsilon}$